

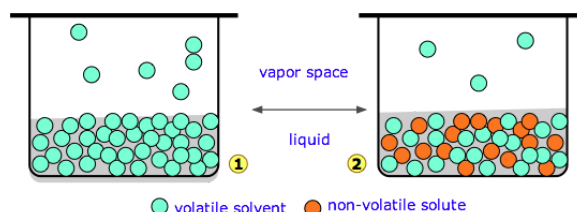
## 8.3: Colligative Properties- Raoult's Law

### Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- State *Raoult's law* in your own words, and explain why it makes sense.
- What do we mean by the *escaping tendency* of a molecule from a phase? How might we be able to observe or measure it?
- Explain why *boiling point elevation* follows naturally from Raoult's law.
- Explaining *freezing point depression* is admittedly a bit more difficult, but you should nevertheless be able to explain how the application of salt on an ice-covered road can cause the ice to melt.

The tendency of molecules to escape from a liquid phase into the gas phase depends in part on how much of an increase in entropy can be achieved in doing so. Evaporation of solvent molecules from the liquid always leads to a large increase in entropy because of the greater volume occupied by the molecules in the gaseous state. But if the liquid solvent is initially “diluted” with solute, its entropy is already larger to start with, so the amount by which it can increase on entering the gas phase will be less. There will accordingly be less tendency for the solvent molecules to enter the gas phase, and so the vapor pressure of the solution diminishes as the concentration of solute increases and that of solvent decreases.



The number  $55.5 \text{ mol L}^{-1}$  ( $= 1000 \text{ g L}^{-1} \div 18 \text{ g mol}^{-1}$ ) is a useful one to remember if you are dealing a lot with aqueous solutions; this represents the concentration of water in pure water. (Strictly speaking, this is the *molal* concentration of  $\text{H}_2\text{O}$ ; it is only the molar concentration at temperatures around  $4^\circ \text{C}$ , where the density of water is closest to  $1.000 \text{ g cm}^{-3}$ .)

Diagram 1 (above left) represents pure water whose concentration in the liquid is  $55.5 \text{ M}$ . A tiny fraction of the  $\text{H}_2\text{O}$  molecules will escape into the vapor space, and if the top of the container is closed, the pressure of water vapor builds up until equilibrium is achieved. Once this happens, water molecules continue to pass between the liquid and vapor in both directions, but at equal rates, so the partial pressure of  $\text{H}_2\text{O}$  in the vapor remains constant at a value known as the *vapor pressure* of water at the particular temperature.

In Figure 8.3.1, we have replaced a fraction of the water molecules with a substance that has zero or negligible vapor pressure — a *nonvolatile solute* such as salt or sugar. This has the effect of diluting the water, reducing its escaping tendency and thus its vapor pressure.

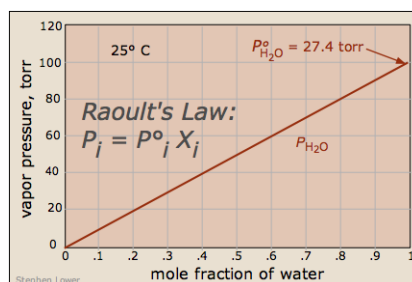


Figure 8.3.1:

What's important to remember is that the reduction in the vapor pressure of a solution of this kind is directly proportional to the fraction of the [volatile] solute molecules in the liquid — that is, to the mole fraction of the solvent. The reduced vapor pressure is given by *Raoult's law*(1886):

$$P = X P^{\circ}$$

$\uparrow$  vapor pressure of solution  
 $\uparrow$  mole fraction of solvent  
 $\uparrow$  vapor pressure of pure solvent

From the definition of mole fraction, you should understand that in a two-component solution (i.e., a solvent and a single solute),

$$\chi_{\text{solvent}} = 1 - \chi_{\text{solute}} \quad (8.3.1)$$

#### ✓ Example 8.3.1

Estimate the vapor pressure of a 40 % (W/W) solution of ordinary cane sugar ( $\text{C}_{22}\text{H}_{44}\text{O}_{11}$ ,  $342 \text{ g mol}^{-1}$ ) in water. The vapor pressure of pure water at this particular temperature is 26.0 torr.

##### Solution

100 g of solution contains  $(40 \text{ g}) \div (342 \text{ g mol}^{-1}) = 0.12 \text{ mol}$  of sugar and  $(60 \text{ g}) \div (18 \text{ g mol}^{-1}) = 3.3 \text{ mol}$  of water. The mole fraction of water in the solution is

$$\frac{3.3}{3.3 + 0.12} = 0.96 \quad (8.3.2)$$

and its vapor pressure will be  $0.96 \times 26.0 \text{ torr} = 25.1 \text{ torr}$ .

#### ✓ Example 8.3.2

The vapor pressure of water at  $10^{\circ} \text{C}$  is 9.2 torr. Estimate the vapor pressure at this temperature of a solution prepared by dissolving 1 mole of  $\text{CaCl}_2$  in 1 L of water.

##### Solution

Each mole of  $\text{CaCl}_2$  dissociates into one mole of  $\text{Ca}^{2+}$  and two moles of  $\text{Cl}^{-}$ , giving a total of three moles of solute particles. The mole fraction of water in the solution will be

$$\frac{55.5}{3 + 55.5} = 0.95 \quad (8.3.3)$$

The vapor pressure will be  $0.95 \times 9.2 \text{ torr} = 8.7 \text{ torr}$ .

Since the sum of all mole fractions in a mixture must be unity, it follows that the more moles of solute, the smaller will be the mole fraction of the solvent. Also, if the solute is a salt that dissociates into ions, then the proportion of solvent molecules will be even smaller.

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